Claims

1. A compound of the formula

$$A_1 - N_1 \longrightarrow R_3 \longrightarrow R_3 \longrightarrow R_2 \longrightarrow N_1 \longrightarrow N_1 \longrightarrow N_2 \longrightarrow N_2 \longrightarrow N_1 \longrightarrow N_2 \longrightarrow N_2 \longrightarrow N_1 \longrightarrow N_2 \longrightarrow N_2$$

in which

R₁ represents hydrogen, substituted or unsubstituted C₁-C₈alkyl, substituted or unsubstituted C₁-C₈alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ and R_{3a} each, independently of the other, represent hydrogen, a C₁-C₄alkyl group, which may be substituted or unsubstituted, halogen, hydroxy, substituted or unsubstituted C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl and each of the residues

A₁ and A₂, independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2)

in which

 X_1 represents C_1 - C_4 alkyl, or phenyl which is unsubstituted or monosubstituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or halogen and

X₂ represents phenyl which is unsubstituted, mono-, di- or trisubstituted by one or two SO₃H, SO₂NHC₁-C₄ alkyl groups which alkyl groups may be substituted, SO₂C₁-C₄alkyl, C₁-C₄substituted or unsubstituted alkyl, hydroxy, C₁-C₄alkoxy, halogen, CF₃, NH₂, NHCOC₁-C₄alkyl, NHCOOC₁-C₄alkyl, NHCOOC₁-C₄alkyl, NHCONHC₁-C₄alkyl, CO₂H, CONHC₁-C₄alkyl or NO₂;

a 1- or 2-naphthyl residue which is unsubstituted or substituted by one or two SO₃H, SO₂NHC₁-C₄alkyl, carboxy, CONHC₁-C₄alkyl, carboxyC₁-C₄alkyl or carboxyaryl groups or a 5- or 6-membered heterocyclic ring containing 1-3 heteroatoms and which may be benzannelated and be further substituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen and which may be attached to the NH-atom in formula (2) either via the hetero- or benzo-nucleus, in the case of benzannelated heterocycles;

a derivative of barbituric acid of the formula

$$- \bigvee_{O} \stackrel{H}{\longrightarrow} Y \qquad (3),$$

in which

Y represents O, NCN or NCONH₂;

a 2,4,6-triaminopyrimidine derivative;

a pyridone derivative of the formula

$$Q_1$$
 Q_2
 Q_4
 Q_3
 Q_3
 Q_3

in which

- Q₁ represents hydrogen, hydroxy, C₁-C₂alkyl, hydroxyethyl, 2-(C₁-C₂alkoxy)alkyl, C₁-C₂alkoxy, COOH, CONH₂ or COOC₁-C₂alkyl,
- Q₂ represents hydrogen, CN, CONH₂, halogen, SO₃H or C₁-C₂alkyl which is unsubstituted or substituted by hydroxy, phenyl or SO₃H,
- Q₃ represents hydrogen, phenyl, C₁-C₂alkylphenyl, cyclohexyl or C₁-C₄alkyl which is unsubstituted or substituted by hydroxy, CN, C₁-C₂alkoxy or SO₃H and
- Q₄ represents hydrogen or hydroxy;

an aminopyrazole or a pyrazolone derivative of formula

in which

 R_4 represents hydrogen, substituted or unsubstituted C_1 - C_4 alkyl, C_2 - C_4 alkenyl,NHCO C_1 - C_4 alkyl or CO_2H , each

 R_5 and R_6 , independently of the other, represent hydrogen, halogen, C_1 - C_4 alkyl, SO_3H or CO_2H and

R₇ represents hydrogen or C₁-C₄alkyl;

a benzoic acid derivative of formula

in which

 R_7 represents hydrogen or $C_1\text{-}C_4\text{alkyl}$ and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

R₉ and R₁₀, each one independently of the other, represent hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen, NH₂, NHCO C₁-C₄alkyl, NO₂, SO₃H, CO₂C₁-C₄alkyl or CONHC₁-C₄alkyl groups,

with the proviso that in compounds of formula

$$A_1 - N_1 - N_2$$

$$R_{3a} - N_3 - N_4$$

$$R_1 - N_1 - N_4$$

if

 R_1 , R_2 , R_3 and R_{3a} each, independently of the others, are hydrogen or SO_3H , then A_1 and A_2 are not both a 1-phenyl or 1-sulphophenyl-3-methyl-5-aminopyrazole residue, or, if

R₁, R₂, R₃ and R_{3a} represent hydrogen and

A₁ is a residue of formula (9) in which

R₇ represents hydrogen or methyl, then

A₂ does not represent a 1-phenyl or 1-sulphophenyl-3-methyl- or 3-carboxy pyrazol-5-one residue

or, if

R₁, R₃ and R_{3a} are hydrogen and R₂ is SO₃H and one of

A₁ and A₂ represents a 1-sulphophenyl-3-methyl pyrazol-5-one residue, then the other is not a residue of formula (11) in which both

R₉ and R₁₀ are hydrogen, or if

A₁ represents a 1-nitrophenyl-, a 1-phenyl- or an unsubstituted 3-methyl pyrazol-5-one residue.

A₂ is not a residue of formula (9) in which R₇ represents hydrogen, or if

R₁, R₃ and R_{3a} represent hydrogen, R₂ is CO₂H and

A₁ represents a residue of formula (9), in which R₇ is hydrogen,

A₂ is not a residue of formula (2) or formula (7);

in compounds of the formula

if

 R_2 represents CO_2H , R_3 represents hydroxy or methoxy and R_{3a} represents hydrogen, A_1 and A_2 do not represent residues of formulae (2) or (7) and, in compounds of the formula

if

 R_2 represents SO₃H and R_3 and R_{3a} both represent hydrogen A₁ and A₂ are not both 2,4-dihydroxyphenyl.

- 2. A compound of formula (1), according to claim 1, which contains a total number of two, three or four SO₃H and/or CO₂H groups.
- 3. A compound of the formula

$$A_1 - N_1 \qquad Q \qquad R_2 \qquad (13),$$

$$R_{3a} \qquad N_1 \qquad N_2 \qquad (13),$$

according to claims 1 or 2, in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined in claim 1.

4. A compound of formula (13), according to claim 3, in which

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2)

in which

X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H,

C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

a pyridone derivative of the formula

$$Q_1$$
 Q_2
 Q_4
 Q_3
 Q_3
 Q_3
 Q_4
 Q_3

in which

Q₁ represents C₁-C₂alkyl,

Q2 represents CN, CONH2 or CH2SO3H,

Q₃ represents C₁-C₂alkyl and

Q₄ represents hydroxy;

an aminopyrazole or a pyrazolone derivative of formula

in which

R₄ represents C₁-C₄alkyl or CO₂H,

 R_{5} represents hydrogen, halogen, $C_{1}\text{-}C_{4}alkyl,\,SO_{3}H$ or $CO_{2}H$ and

R₆ represents hydrogen;

a benzoic acid derivative of formula

in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

 A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

 R_{9} represents hydrogen, $C_{1}\text{-}C_{4}\text{alkyl},\,C_{1}\text{-}C_{4}\text{alkoxy},\,\text{hydroxy},\,\text{halogen or SO}_{3}\text{H}$ and

R₁₀ represents hydrogen.

5. A compound of formula

according to claims 1 or 2, in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

 R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

 R_{3a} represents hydrogen or NH_2 and

A₁ and A₂ are as defined in claim 1.

6. A compound of formula (14), according to claim 5, in which

 R_3 and R_{3a} both represent hydrogen and

 A_1 and A_2 , each one independently of the other, is derived from a coupling component selected from the group consisting of

an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2) ,

in which

X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H,

C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid:

2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

in which

R₄ represents C₁-C₄alkyl or CO₂H,

 R_{5} represents hydrogen, halogen, $C_{1}\text{-}C_{4}alkyl,\,SO_{3}H$ or $CO_{2}H$ and

R₆ represents hydrogen;

a benzoic acid derivative of formula

in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

 R_9 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen or SO_3H and R_{10} represents hydrogen.

7. A compound of formula

$$A_{1}-N$$

$$R_{3a}$$

$$N$$

$$R_{1}$$

$$N=N$$

$$A_{2}$$

$$A_{2}$$

$$A_{3}$$

$$A_{3}$$

$$A_{4}$$

$$A_{2}$$

$$A_{3}$$

according to claims 1 or 2, in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

 R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined in claim 1.

8. A compound of formula (15), according to claim 7, in which

 R_3 and R_{3a} both represent hydrogen and

 A_1 and A_2 , each one independently of the other, is derived from a coupling component selected from the group consisting of

an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2)

in which

X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H,

C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

$$R_4$$
 N
 N
 NH_2
 R_6
 R_5
 R_5
 R_5
 R_5
 R_7
 R_8
 R_8
 R_8
 R_8
 R_8

in which

R₄ represents C₁-C₄alkyl or CO₂H,

 R_{5} represents hydrogen, halogen, $C_{\text{1}}\text{-}C_{\text{4}}\text{alkyl}\text{, }SO_{\text{3}}\text{H or }CO_{\text{2}}\text{H and }$

R₆ represents hydrogen;

a benzoic acid derivative of formula

in which

 $\ensuremath{\mathsf{R}}_7$ represents hydrogen or $\ensuremath{\mathsf{C}}_1\text{-}\ensuremath{\mathsf{C}}_4\ensuremath{\mathsf{alkyl}}$ and

R₈ represents hydrogen or hydroxy or

 A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula

$$R_{9}$$
 OH (11) or R_{10} OH (12),

in which

 R_9 represents hydrogen, $C_1\text{-}C_4$ alkyl, $C_1\text{-}C_4$ alkoxy, hydroxy, halogen or SO_3H and R_{10} represents hydrogen.

9. A compound of formula

according to claims 1 or 2, in which

 R_1 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or SO_3H_1

R₂ represents SO₃H or CO₂H,

 R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined in claim 1.

10. A compound of formula (16), according to claim 9, in which

 $R_{\rm 3}$ and $R_{\rm 3a}$ both represent hydrogen and

 A_1 and A_2 , each one independently of the other, is derived from a coupling component selected from the group consisting of

an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2) ,

in which

X₁ represents C₁-C₄alkyl, and

 X_2 represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO_3H ,

 C_1 - C_4 alkyl, hydroxy, C_1 - C_4 alkoxy, halogen or CO_2H ;

barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid:

an aminopyrazole or a pyrazolone derivative of formula

in which

R₄ represents C₁-C₄alkyl or CO₂H,

 R_{5} represents hydrogen, halogen, $C_{1}\text{-}C_{4}\text{alkyl},\,SO_{3}\text{H}$ or $CO_{2}\text{H}$ and

R₆ represents hydrogen;

a benzoic acid derivative of formula

$$O$$
OH O OH

in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

 A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

 R_9 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen or SO_3H and R_{10} represents hydrogen.

11. A process for the preparation of a compound of formula (1), according to claim 1, by tetrazotisation of a diaminobenzanilide derivative of the formula

in which R_1 , R_2 , R_3 and R_{3a} are as defined in claim 1, and sequential coupling with a coupling component of the formula A_1H or A_2H , followed by coupling with a coupling component of the formula A_2H or A_1H , A_2 and A_3 being as defined in claim 1.

12. A compound of the formula

$$\begin{array}{c|c}
 & O & O \\
 &$$

- 13. A process for the preparation of compound (18), according to claim 12, by reaction of 2-methoxy-4-nitroaniline-5-sulphonic acid with the appropriate nitrbenzoyl halide, followed by reduction of the resulting dintrobenzanilide.
- 14. Use of the compound of formula (18), according to claim 12, for the preparation of the appropriate compound of formula (1), according to claim 1.
- 15. Use of the compound of formula (1), according to claim 1, for dyeing natural or synthetic materials.
- 16. A solid dye preparation for dyeing paper, comprising a compound of the formula (1) according to claim 1, and, optionally, further auxiliaries.
- 17. Aqueous solutions for dyeing paper, comprising a compound of the formula (1), according to claim 1, and, optionally, further auxiliaries.

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- 18. Aqueous solutions according to claim 17 containing, as further auxiliaries, solubilizers and/or organic solvents.
- 19. Paper which is dyed with a compound of the formula (1), according to claim 1, in the form of a solid dye preparation, according to claim 16, or an aqueous solution, according to claim 17.